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Discharge Behavior of the AgO-Ag Electrode

E. A. Butler

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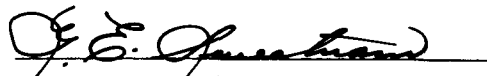
**JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA**

December 22, 1963

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Discharge Behavior of the AgO-Ag Electrode

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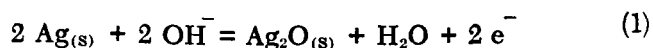
ABSTRACT

The production of gas by AgO electrodes and by AgO powder and pellets in 40% KOH at 25°C was investigated. Little gas was evolved by any form of AgO during chemical reaction or electrochemical reaction, provided that the temperature of the material remained in the vicinity of 25°C. Gas was released by electrodes which had been treated at 100°C and was probably occluded oxygen produced by chemical decomposition of AgO. There was no evidence that gassing was affected by the electrode potential. Examination of partially discharged plates indicated that the electrochemical reaction occurred preferentially at physical discontinuities.

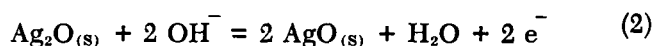
I. INTRODUCTION

During various tests and experimental procedures on silver oxide-zinc batteries conducted at the Jet Propulsion Laboratory (JPL), certain phenomena were noted which were unexplainable and which seemed sufficiently important to warrant further study. These may be summarized as follows:

1. The silver-zinc alkaline cell is characterized by two voltage plateaus on charge and discharge. The open-circuit voltages of these plateaus are approximately 1.60 and 1.85 v. The half-reaction which occurs at the silver electrode during the first state of charge is assumed to be



and that during the second stage is written as



Upon discharge, the reactions are written as Eq. (2), reversed, followed by Eq. (1), reversed.

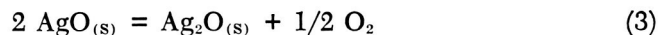
Although one would expect reactions (1) and (2) to result in two voltage plateaus of identical length during discharge, in practice less than half of the cell's capacity is delivered at the higher voltage, with the remainder being available at the lower voltage. Some observers (Ref. 1) have reported that this loss of capacity at the higher voltage was just compensated for by an increase

in capacity at the lower voltage. Others (Ref. 2) have noted some loss in total capacity.

2. Certain silver-zinc cells were found to evolve gas rapidly upon activation and normal discharge (Ref. 3). Where these cells were sealed, pressures in some cases exceeded 60 psi, although the buildup of pressure varied greatly from cell to cell. Preliminary experiments showed that most of the gas originated on the silver-oxide electrode.

3. Very slow decomposition of AgO was evident from the fact that unactivated cells stored in a dry atmosphere

over a period of 1 to 2 yr lost virtually all capacity at the higher voltage plateau. Amlie and Rüetschi (Ref. 4) observed a slow decomposition reaction of AgO in KOH solution. This occurs in addition to any electrochemical reaction such as Eq. (1) or Eq. (2) and produces oxygen



Because of these observations, work was undertaken in an attempt to determine the nature and the cause of the gas-producing reactions at the silver electrode.

II. EXPERIMENTS

A. Preparation of AgO

AgO was prepared chemically by the method of Bailar (Ref. 5). It was prepared also electrolytically by oxidation of sintered silver plates in 25% KOH at a nominal current density of 0.02 amp/in.² AgO was analyzed for oxidizing capacity by the method of Dutta (Ref. 6).

B. Decomposition of AgO in 40% KOH Solution

Measurements similar to those of Amlie and Rüetschi (Ref. 6) were extended to include AgO taken from available commercial electrodes. The procedure followed was to weigh 0.500 g of AgO into the reaction tube (Fig. 1), fill the tube with 40% KOH solution, and attach the

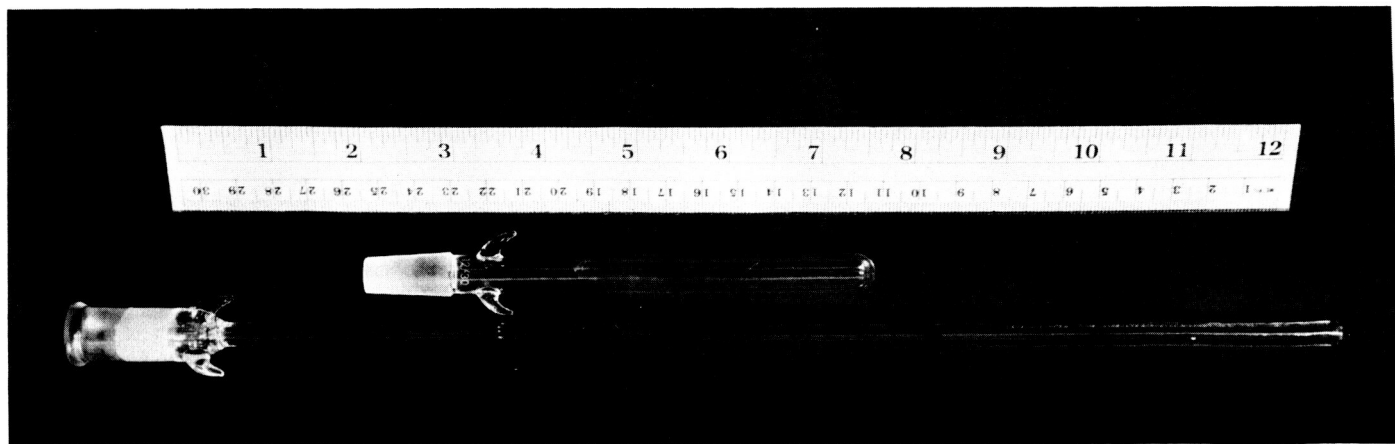


Fig. 1. Gas measuring reaction tube

measuring pipet by means of the ground glass joint, coated with silicone grease. The joint was then sealed with paraffin and the tube immersed in a water bath thermostatically controlled at $25.0 \pm 0.02^\circ\text{C}$. Since some of the samples gassed profusely upon first being wetted with the KOH solution, volume readings were begun only after a 24-hour equilibration period.

C. Gas Evolution on Discharge

A cell was constructed of an AgO cathode and Zn anode in 40% KOH. A flattened funnel was connected to a

50-ml buret and clamped in place over the AgO electrode (Fig. 2). The discharge reaction was carried out at a constant 1.0 amp, which was controlled by a Perkin Model TVCR 040-30 power supply. Both commercial and laboratory prepared plates were used.

D. Electromotive Force Measurements

Experiments were done in the apparatus shown in Fig. 3. The cell chamber was a 25-cm desiccator with a 10-cm thick foamed-in-place polyurethane insulator on the lid. The central electrode was the Hg/HgO electrode, while the others were Ag/AgO. The main body of the desiccator was immersed in a thermostatically controlled bath, which was light-tight to prevent photochemical reaction of the silver species. Teflon stoppered bridges containing 40% KOH were used to connect the cell compartments. The stoppers were left in the just-open position to give electrical contact through the bridge while preventing solution flow. All potential measurements were made with a Leeds and Northrop K-3 potentiometer.

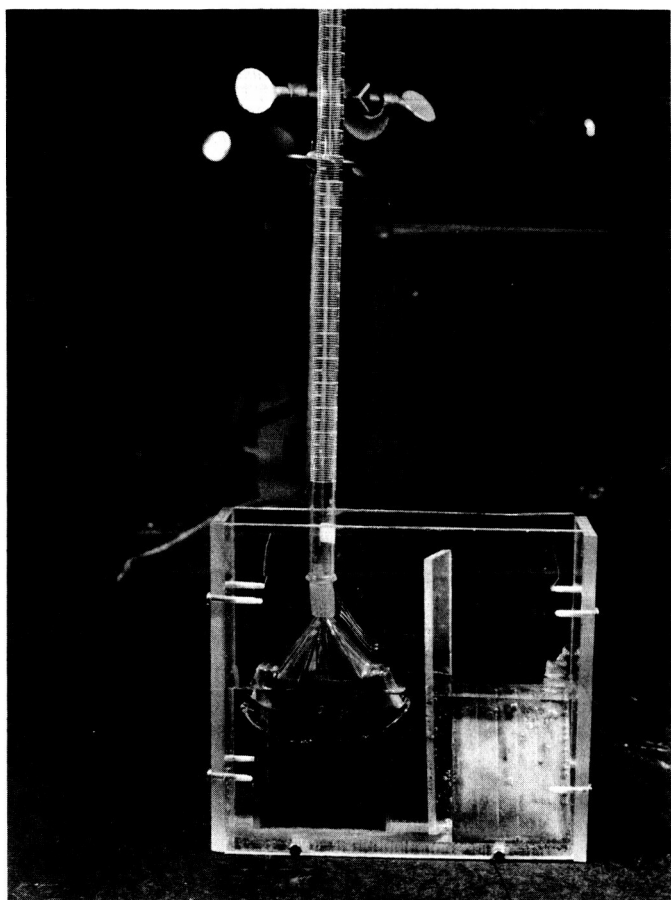


Fig. 2. Cell for gas collection during discharge



Fig. 3. Cell chamber for EMF measurements

III. RESULTS AND DISCUSSION

A. Decomposition of AgO in KOH

The results of experiments on the rate of decomposition of AgO in KOH solution are shown in Table 1 and Fig. 4. The rates obtained with commercially pressed AgO plates are seen to be erratic (upper three plots). Reproducible results could not be obtained from such material. On the other hand, consistent rates were obtained with chemically prepared AgO, and the rate did not depend upon whether the AgO was in powder or pellet form. Furthermore, as Fig. 4 indicates, the rate

obtained from electrochemically prepared AgO was the same as that of the chemically prepared material.

At the measured rate, the complete decomposition of AgO in 40% KOH solution at 25°C would require about 1500 days.

B. Gas Evolution on Discharge

The rate of evolution of gas from the AgO plate upon discharge was found to vary greatly from plate to plate

Table 1. Rates of oxygen evolution from decomposition of AgO in 40% KOH at $25.00 \pm 0.02^\circ\text{C}$

AgO type	Volume, ml							
	72 hr	96 hr	121 hr	170 hr				
Chemically prepared AgO; powdered form:								
Sample I	0.080	0.094	0.114	0.156				
Sample II	0.076	0.090	0.110	0.150				
Sample III	0.078	0.080	0.098	0.134				
Chemically prepared AgO; pellet form:	24 hr	43 hr	69 hr	140 hr	162 hr			
Sample I	0.016	0.034	0.059	0.118	0.144			
Sample II	0.014	0.034	—	—	—			
Chemically prepared AgO (from commercial pressed plate):	23 hr	46 hr	69 hr	93 hr	117 hr	121 hr	143 hr	167 hr
Sample I	—	—	0.193	0.263	0.330	—	—	—
Sample II	—	—	0.302	0.380	0.449	—	—	—
Sample III	0.043	0.066	—	—	—	0.191	0.235	0.289
Electroformed AgO:	25 hr	48 hr	121 hr	144 hr	169 hr			
Sample I	0.024	0.044	0.104	0.120	0.138			
Sample II	0.022	0.054	0.116	0.134	0.143			
Sample III	0.026	0.046	0.118	—	—			

Table 2. Oxygen evolved upon discharge of Ag, AgO plates at 1.0 amp
(total plate area approximately 20 in.²)

AgO type	Volume, ml									
Chemically prepared AgO (commercial), molded with heat and pressure:	0.5 hr	1.0 hr	1.5 hr	2.0 hr	2.5 hr	3.0 hr	3.5 hr	5.0 hr	5.5 hr	6.5 hr
	5.0	8.5	11.9	14.3	—	—	—	—	—	—
	4.5	—	15.8	21.0	—	29.0	—	—	—	—
	2.8	5.6	—	10.3	—	—	14.8	—	—	—
	3.2	—	8.4	10.3	—	14.0	16.3	21.0	—	—
	4.3	11.9	14.4	—	14.5	—	—	—	30.2	33.6
Chemically prepared AgO (commercial), molded with heat and pressure; completely discharged, then electroformed:	0.5 hr	1.0 hr	1.5 hr	2.5 hr	4.5 hr					
	0	0	0	0	0.1					
Chemically prepared AgO (commercial), molded with heat and pressure; reduced at 600°C, then electroformed:	1 hr	2 hr	3 hr	4 hr	5 hr					
	0	0	0.1	0.1	0.1					
Electroformed AgO:	0.5 hr	1.0 hr	1.5 hr	2.0 hr	2.5 hr	3.5 hr	4.0 hr			
	0	0.1	0.1	0.2	0.3	0.5	0.6			
	0	—	0	—	—	0	0			
Electroformed AgO; then heated to 100°C for 24 hr:	1 hr	2 hr	3 hr							
	7.0	13.5	19.0							

(Table 2 and Fig. 5). As was true with the decomposition reaction, reproducible values could not be obtained in the case of commercial plates pressed from AgO on Ag grids. In addition to the large and variable volumes of gas evolved from such plates on discharge, there was gas evolution to the extent of 3 to 10 ml when the plates were first wetted with the KOH solution. This was in sharp contrast to electrochemically prepared plates which did not gas upon being wetted, and which gassed very little on discharge (Table 2 and Fig. 5).

The gas evolved from the silver plate upon both wetting and discharge was analyzed mass-spectrometrically and found to be oxygen with a trace of hydrogen. Since the electrode is cathodic during discharge, this suggests strongly that the oxygen is not electrochemically formed.

Complete discharge of a pressed AgO on Ag plate followed by electrochemical oxidation produced a plate which did not gas significantly on subsequent discharge. The same was true of such a plate that was reduced to

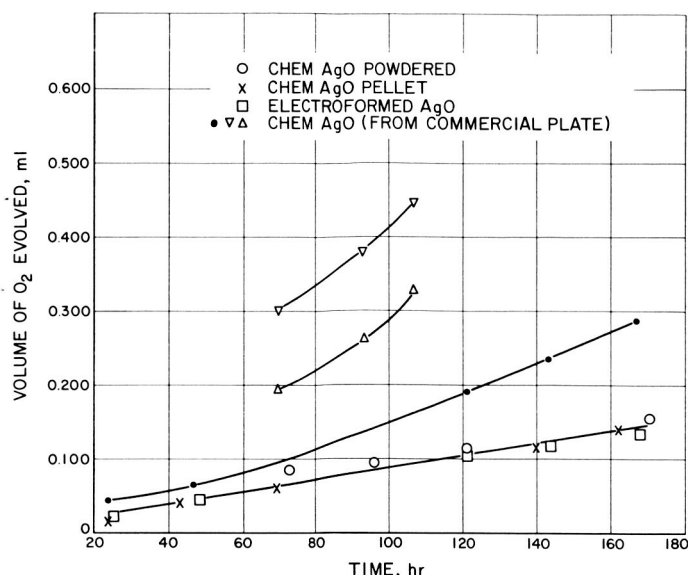


Fig. 4. Oxygen evolution (AgO in 40% KOH at 25°C)

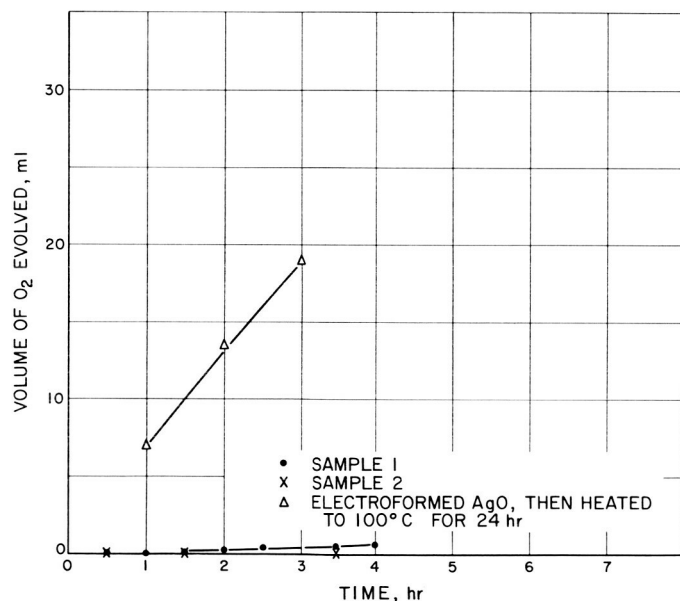


Fig. 5. Oxygen evolved upon discharge of Ag,AgO plates at 1.0 amp

Ag by being heated to 600°C for 3 min and then electrochemically oxidized (Table 2).

It was found that an electrochemically oxidized plate could be caused to gas upon being wetted and discharged, if, prior to these treatments, it had been heated to 100°C. The quantity of gas evolved was a function of the length of time of heating. Data for such a plate heated for 24 hr are given in Fig. 6.

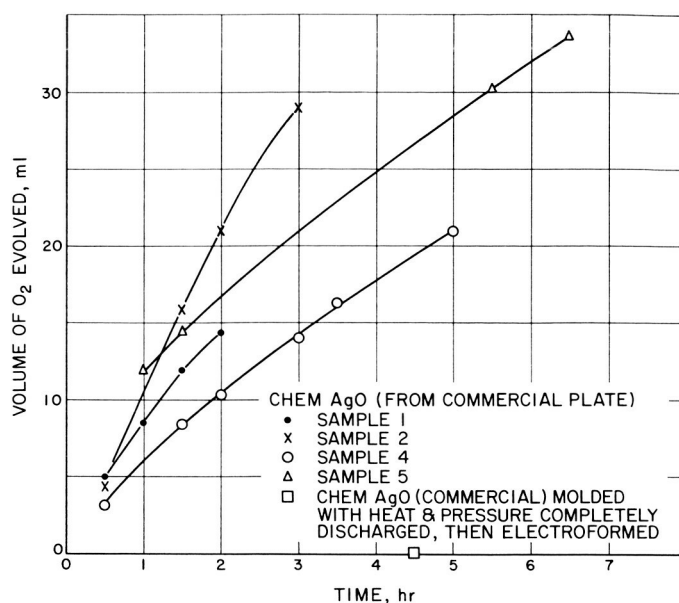


Fig. 6. Effect of high temperature on oxygen evolution from electroformed AgO plates during discharge

Exploratory experiments, in which electroformed AgO plates were heated to 100°C in 40% KOH solution in a bomb fitted with a pressure gauge (Fig. 7), indicate that the KOH solution does not inhibit the gas forming reaction, although the gas produced under these conditions is probably not occluded by the silver oxide.

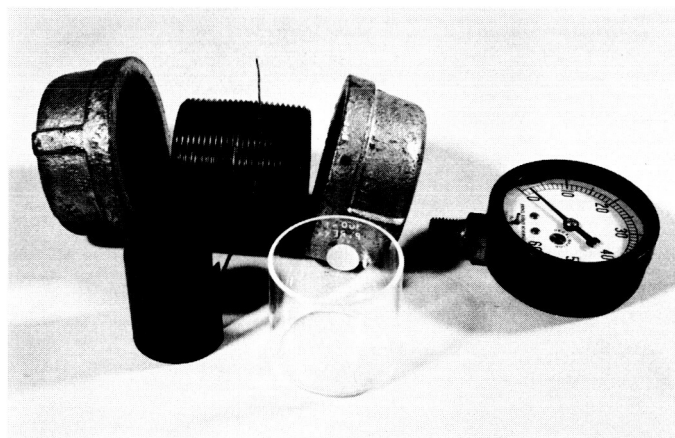


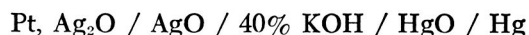
Fig. 7. Bomb for heating AgO plate in KOH

Experiments with chemically prepared AgO indicated that, in 1 hr at 145°C, approximately one-half of the AgO is reduced to Ag₂O, and that, in 24 hr, the reduction to Ag₂O is complete. In 48 hr, the reduction to Ag did not appear to be significant.

From these experiments, it is concluded that the gas evolved from certain AgO-Ag plates upon being wetted or discharged is oxygen occluded by the silver oxide, which oxygen was produced when the AgO was heated as the plate was pressed. The plate can be made of chemically or electrolytically prepared AgO, and will not gas significantly unless the material has been heated. When heated, it decomposes by the reaction shown in Eq. (3), but at a rate which is orders of magnitude higher than in KOH solution at 25°C. The mechanism of these reactions has not been studied yet.

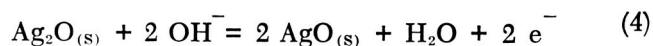
C. Electromotive Force Measurements

During the early period of this work, it was postulated that the variations in gassing rates from AgO-Ag plates might be caused by variations in electrode potentials. Differences as high as 72 mv were found in the plates of an individual commercial cell. Therefore, consideration was given to the measurement of the potential of the cell



at 25°C.

Bonk and Garrett (Ref. 7) have measured E° for the half-cell.



They did not make measurements, however, in the high KOH concentrations, which obtain in the silver-zinc cell.

The AgO, Ag₂O electrodes were prepared in two different ways: (1) Sintered silver on silver grid was oxidized electrolytically to AgO and was allowed to stand in 40% KOH for 24 hr prior to the making of potential measurements. The stand period gave time for some decomposition to Ag₂O. (2) A platinum helix was immersed in a slurry of chemically prepared AgO and Ag₂O in 40% KOH. Stability and reproducibility to ± 1 mv or better, were obtained by either of these methods, with cell voltages being 0.502 v. However, variations of the order of 3 mv were encountered in the use of the HgO, Hg electrode. This problem has not yet been solved. No evidence was found to support the argument that oxygen evolution was related in any way to the electrode potential.

D. Reaction Geometry on the AgO-Ag Electrode

Examination of partially discharged plates indicates that reduction occurs preferentially in the immediate

vicinity of the grid wires, unless some other surface discontinuities are produced in the fabrication or handling of the plates, whereupon reduction occurs preferentially at these regions. Figure 8 shows a plate formed by pressing AgO on a silver grid in which the plate has been grooved by the process. Figure 9 shows a similar plate which has been partially discharged. The grooves are seen to be preferential sites for the reduction of the AgO, as are cracks in the plate (lower left) caused by rough handling. On the other hand, Fig. 10 shows the preferential reduction at the grid wires where the plate surface is free of macroscopic imperfections. A cross-sectional view of a partially discharged plate shows that reduced silver always appears to be in contact with the grid (Fig. 11) and that the growth of reduced areas seems to occur at the AgO-Ag interfaces.

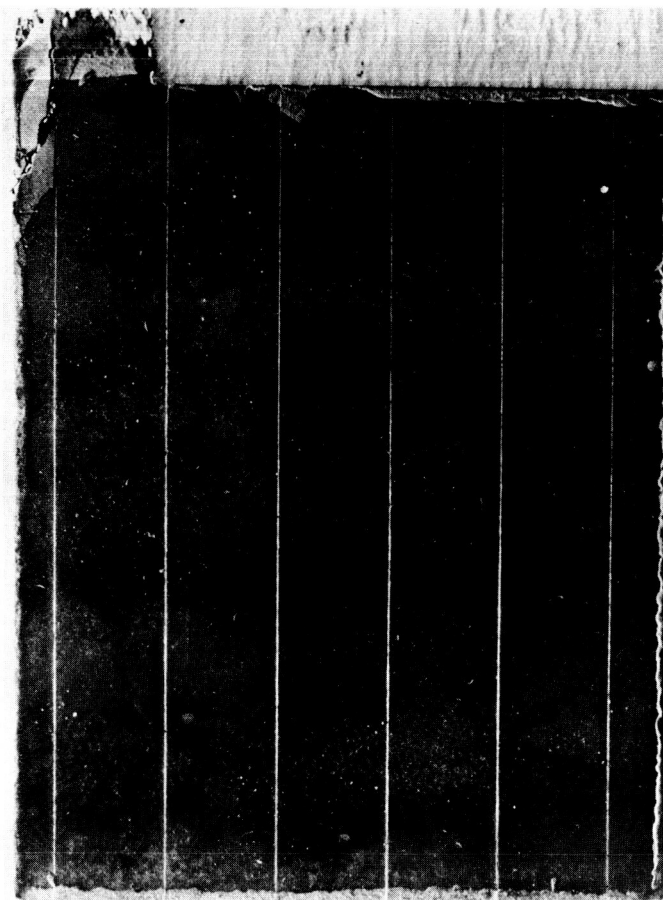


Fig. 8. Pressed AgO plate before discharge

The above observations seem to indicate that the current density of a fully charged AgO plate must be considered in terms of the total *grid* surface area, and that

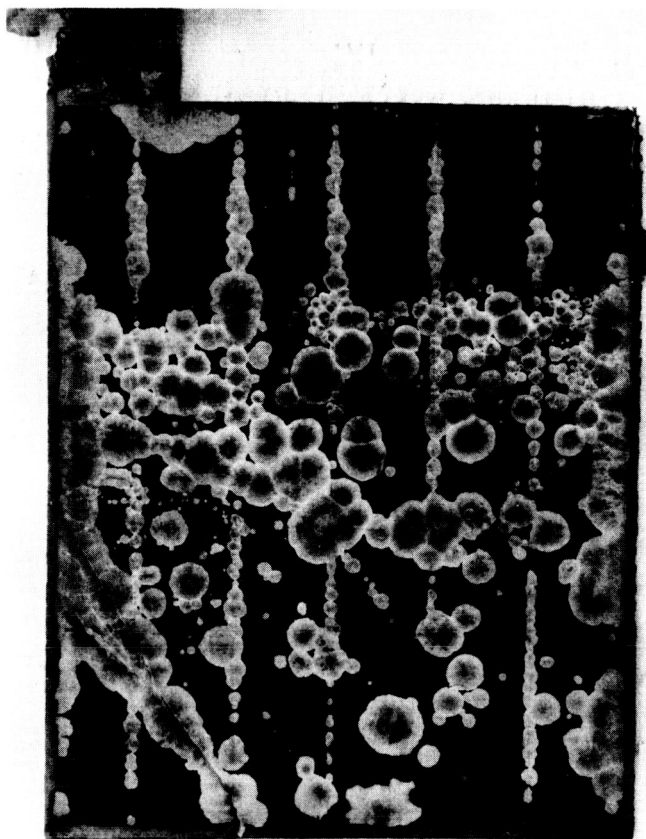


Fig. 9. Pressed AgO plate after partial discharge

the effective plate area constantly changes as the reduced silver regions increase. If this is the case, changing the porosity of the AgO plate would have very little effect on initial current density, and may be important only in terms of plate resistance and the effect on the distribution of reduced silver as the discharge proceeds.

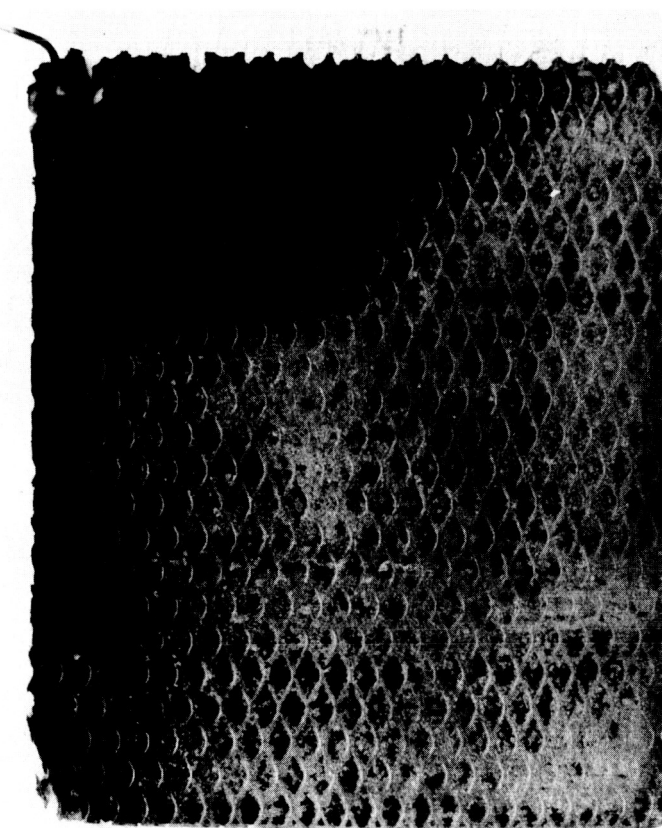


Fig. 10. Smooth AgO plate after partial discharge

Studies of the geometry of reaction on the electrode are being continued in an effort to understand the factors which determine the relative reactivity of various sites on the electrode, and, thereby, to be able to control better the uniformity of reduction and oxidization of the electrode during its cycling.

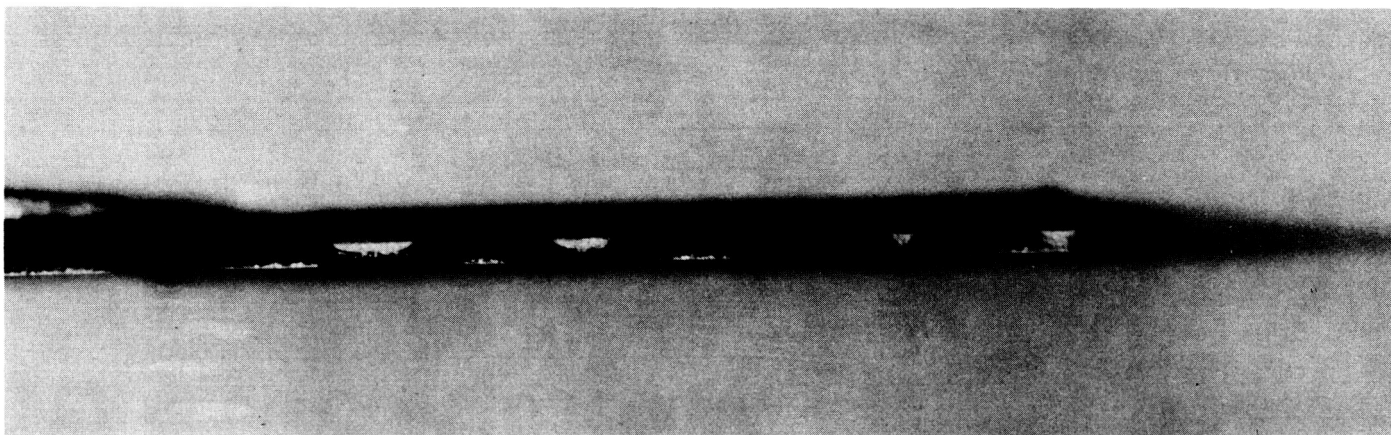


Fig. 11. Cross section of pressed AgO plate after partial discharge

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